

# Resonant X-rays at the Cu L-edge as a momentum dependent probe of the magnetic excitation spectrum in cuprates

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We show that, contrary to common lore, in resonant inelastic x-ray scattering (RIXS) at the copper L- and M-edge direct spin-flip scattering is in principle allowed. We demonstrate how this possibility can be exploited to probe the momentum dependent magnetic properties of cuprates such as the high  $T_c$  superconductors and compute in detail the relevant local and momentum dependent magnetic scattering amplitudes, which we compare to the elastic and  $dd$ -excitation scattering intensities. For cuprates these results put RIXS as a technique on the same footing as neutron scattering.

*Introduction.* In recent years the experimental technique of resonant inelastic x-ray scattering (RIXS) has made tremendous progress in terms of energy and momentum resolution [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11]. RIXS is particularly apt to probe the properties of strongly correlated electrons, for instance the ones of the transition metal oxides [1, 2]. With an incoming x-ray of energy  $\omega_{in}$  first an electron is resonantly excited from a core level into the valence shell. Subsequently one measures the energy  $\omega_{out}$  of the outgoing x-ray resulting from the recombination of the core hole with a valence electron. Depending on the resonance that the experiment is performed at,  $\omega_{in}$  corresponds to the transition metal K-edge ( $1s \rightarrow 4p$ ), L-edge ( $2p \rightarrow 3d$ ) or M-edge ( $3p \rightarrow 3d$ ). Compared to the many other photon scattering techniques, RIXS has the advantage that there is no core hole present in the final state, so that the energy lost by the scattered photon at a transition metal L- or M-edge is directly related to electronic excitations within the strongly correlated  $3d$  valence bands. The chemical selectivity and bulk sensitivity of RIXS allows the study of the electronic and magnetic properties of, for example, complex and nanostructured materials that might be inaccessible with non-resonant techniques.

RIXS has been much used in transition metal oxides to study local transitions, such as  $dd$ -excitations in cuprates [3, 4, 5] and spin flips [6, 7] in NiO. Although interesting in themselves, these experiments do not exploit a unique feature of RIXS: it allows the measurement of the *dispersion* of excitations by determining both momentum change and energy loss of the scattered x-ray photons. Such a capability is far beyond the possibilities of traditional low energy optical techniques, which are constrained to zero momentum transfer because, as opposed to high energy x-rays, photons in the visible range carry negligible momentum. This asset has already been exploited to determine the momentum dependence of charge [8, 9, 10], bimagnon [11, 12, 13, 14] and orbital

excitations [15, 16] at Cu K and  $L_3$  edges. In this Letter we show that, contrary to common lore [2, 3, 5, 17], RIXS at the copper L-edge is also a very powerful probe of single-magnon excitations and their dispersions. This is an important result because it puts the technique of L-edge RIXS on, for instance, the high  $T_c$  superconductors, on the same footing as neutron scattering –with the considerable advantage that x-ray scattering requires only small sample volumes.

In the following we will first determine the local spin-flip cross section for a copper  $d^9$  ion in a tetragonal crystal field. This is the familiar case encountered in numerous cuprates, where the only unquenched magnetic moment in the system is the one of a hole occupying a  $x^2-y^2$  orbital. The important observation is that it strongly depends on the spatial orientation of the copper spin whether this local spin-flip process is forbidden or not. In the second part of the Letter we determine the momentum ( $\mathbf{q}$ -) dependence of the magnon cross section for a spin system with collective response. As an example we consider the Heisenberg antiferromagnet, where we find a vanishing of the magnon scattering intensity around the center of the Brillouin zone proportional to  $|\mathbf{q}|$  and strongly peaking of it around the antiferromagnetic wave vector.

*Local spin-flip scattering at Cu L-edge.* From the viewpoint of inelastic magnetic scattering it appears that RIXS and neutron scattering are very different techniques. It is easy to show, for instance, that in transition metal K-edge RIXS single spin-flip scattering is forbidden [12] because of the absence of spin-orbit coupling in the intermediate state. Ever since the seminal work of Kuiper and coworkers [3], more than a decade ago, it is believed that also at the copper L- and M-edge spin-flip scattering is not allowed for  $\text{Cu}^{2+}$  in a tetragonal crystal field, unless the spin-flip excitation is accompanied by a  $dd$ -excitation [2, 5, 17]. Based on a symmetry analysis of the wavefunction of the copper hole, Ref. 17

states that “the reason is that the  $x^2-y^2$  state, a linear combination of atomic  $Y_{2,2}$  and  $Y_{2,-2}$  states, does not allow a direct spin-flip transition”. The observation that the spin-flip excitations are intrinsically entangled with  $dd$ -excitations implies that mapping out momentum dependencies of magnetic excitations with L-edge RIXS would be a hopeless endeavor. As will be clarified shortly, the  $dd$ -excitations act as a momentum sink, which would limit the information that can be gained from RIXS in this case to *momentum averaged properties* of the magnetic excitations, preempting the possibility to observe single magnon dispersions.

We will show in the following, however, that the symmetry analysis on which these assertions rely [5, 17] is incomplete because restricted to directions of the spin moment along an axis that is orthogonal to the  $x^2-y^2$  orbital. In fact we show that *for any other spin orientation direct spin-flip scattering is allowed*. This includes in particular the Néel ordered high  $T_c$  cuprates, where the magnetic moment lies in the plane of the  $x^2-y^2$  orbital: for example in  $\text{La}_2\text{CuO}_4$ ,  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$  and  $(\text{CaSr})\text{CuO}_2$ , [18, 19] spins point along the  $[x, y, z]=[110]$  direction and in  $\text{Nd}_2\text{CuO}_4$  along  $[100]$  and  $[010]$  in alternating planes. [20]

The dependence of the direct spin-flip scattering amplitude on photon polarization, scattering angle and momentum transfer can be computed from the Kramers-Heisenberg expression [21]:  $A_{fi} \propto \sum_n \langle f | \hat{D} | n \rangle \langle n | \hat{D} | i \rangle / (\omega_{\text{det}} - E_n + i\Gamma)$ , where  $A_{fi}$  is the scattering amplitude from initial state  $i$  to final state  $f$ ,  $\omega_{\text{res}}$  is the resonant energy (around 930 eV at the copper  $L_3$ -edge),  $\hat{D}$  the polarization dependent dipole operator,  $\omega_{\text{det}} \equiv \omega_{\text{in}} - \omega_{\text{res}}$  is the detuning away from the resonance,  $|n\rangle$  the intermediate state with energy  $E_n$  (measured with respect to the resonance energy) and  $\Gamma$  the core-hole lifetime. At the copper L-edge we are dealing with the local electronic process  $2p^6 3d^9 \rightarrow 2p^5 3d^{10} \rightarrow 2p^6 3d^{9*}$ , where  $*$  denotes an excited state with a  $dd$ -excitation and/or spin flip. At the  $L_3$  resonance the intermediate states  $|n\rangle$  are just the multiplets corresponding to the four  $J^z = L^z + S^z$  states of the spin-orbit coupled  $2p_{3/2}$  core-hole so that the calculation becomes relatively simple because all paths from the ground state to a given final state interfere with equal weight.

It is easy to see that direct spin-flip excitations are forbidden if the spin of the hole in the  $x^2-y^2 = (Y_{2,2} + Y_{2,-2})/\sqrt{2}$  initial state is aligned along  $[001]$ , which is the situation considered previously [5, 17]. In the first step of the RIXS process a dipole allowed  $2p \rightarrow 3d$  transition creates a core hole in a linear combination of  $Y_{1,1}$  and  $Y_{1,-1}$ , while conserving the spin. In this intermediate state the spin-orbit coupling of the core-hole  $\mathbf{L} \cdot \mathbf{S} = L^z S^z + (L^+ S^- + L^- S^+)/2$  can cause a spin-flip  $S^-$  (or  $S^+$ ) in combination with a raising (or lowering)  $L^+$  (or  $L^-$ ) of the orbital moment. In either case a  $Y_{1,0}$  core-hole state with reversed spin is the result [5, 17, 22]. The last step to end up in a final state with only a spin-

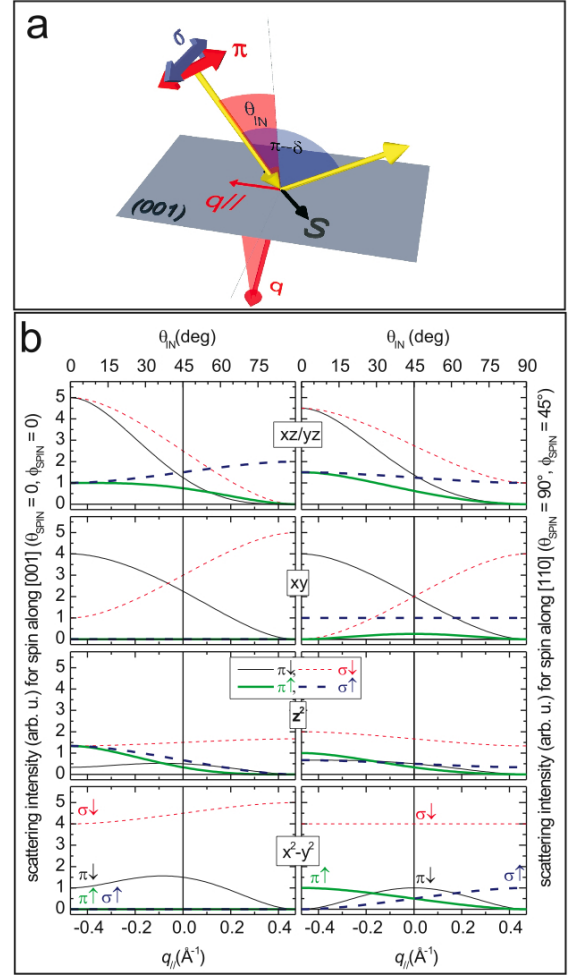


FIG. 1: The  $\text{Cu}^{2+}$   $L_3$  local RIXS cross section for  $\sigma$  and  $\pi$  polarization of the incident beam calculated in the single ion model. The experimental geometry is sketched in panel a: the scattering plane is  $(100)$ , the scattering angle is  $90^\circ$ , the incident photons impinge at an angle  $\theta_{\text{IN}}$  to the  $[001]$  crystallographic direction ( $c$  axis). The spin orientation is varied in the calculation. In panel b, all the possible  $dd$ -excitations plus the spin-flip and the elastic scattering final states are considered, vs  $\theta_{\text{IN}}$  or alternatively the in-plane transferred momentum  $q_{\parallel}$ . We notice that along the  $[100]$  direction the nuclear Brillouin zone boundary is in  $q_{\parallel} \approx 0.826\hbar \text{ \AA}^{-1}$  for  $a = 3.8 \text{ \AA}$  in-plane parameter, typical of cuprates: at  $90^\circ$  scattering Cu  $L_3$  RIXS can explore half of the reciprocal space, but going to backscattering geometry  $q_{\parallel}$  grows considerably and almost all the Brillouin zone can be covered. When the spin is along  $[001]$  the spin flip cross section vanishes (bottom left), but not when the spin is along  $[110]$  (bottom right).

flip excitation, requires the optical decay of the  $Y_{1,0}$   $2p$  core-hole into a  $(Y_{2,2} + Y_{2,-2})/\sqrt{2}$   $3d$  valence band hole. But this transition is dipole forbidden because it requires  $\Delta L^z = 2$ , which thus forbids direct spin-flip scattering completely. According to the same argument, a local spin-flip is allowed if the hole in the final state is any

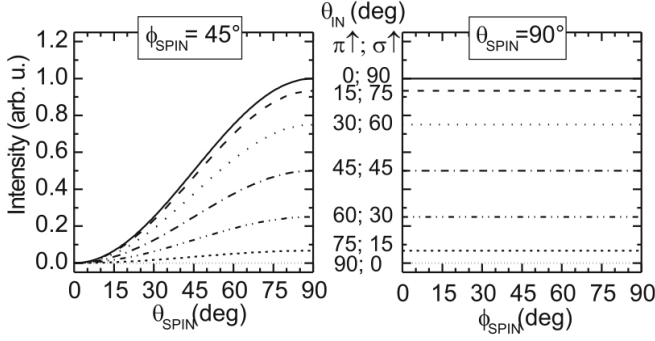


FIG. 2: The dependence of scattering cross section for elastic  $(x^2-y^2)\downarrow$  and spin-flip  $(x^2-y^2)\uparrow$  final states on the atomic spin orientation for selected cases of scattering geometry given by varying  $\theta_{\text{IN}}$  and fixed  $\phi_{\text{IN}} = 0$ .

another orbital than  $x^2-y^2$ .

The situation changes drastically when the local magnetic moment is oriented in the  $x$ - $y$  plane: we will show that now direct spin-flip excitations become allowed. This is best illustrated by a direct calculation of the RIXS amplitudes in the different channels for  $\text{Cu}^{2+}$  in a tetragonal crystal field. We did so for the scattering geometry sketched in Fig. 1a, with fixed scattering angle of  $90^\circ$  and  $\pi$  ( $\sigma$ ) linear polarization of the incident photons parallel (perpendicular) to the scattering plane. In this geometry  $\theta_{\text{IN}}$  is the azimuthal angle between incident beam and  $[001]$  axis. In Fig. 1b the exact polarization and momentum dependent RIXS matrix elements for all possible final states and for an initial magnetic moment either along  $[001]$  (left panels) or along  $[110]$  (right panels) are shown. The computed spin flip and  $dd$ -excitation cross section start from a local ground state  $(x^2-y^2)\downarrow$ , so that  $(x^2-y^2)\uparrow$  is a final state with a spin flip excitation only. On the bottom axis of Fig. 1b is the momentum transfer in the experimental geometry at  $\omega_{\text{in}} = 930$  eV. From the lower panels at the left and right it is clear that for a spin along  $[110]$  the spin flip cross section is allowed for both  $\sigma$  and  $\pi$  polarizations, whereas it is in all cases forbidden for a spin along  $[001]$ . It is interesting to note that for the  $\sigma$  polarization the elastic peak is more than 4 times stronger than the spin-flip scattering channel, whereas for  $\pi$  the two intensities are similar. The direct spin-flip and elastic cross section for a generic spin direction, characterized by the Euler angles  $(\theta_{\text{spin}}, \phi_{\text{spin}})$  are shown in Fig. 2 for a number of azimuthal angles  $\theta_{\text{IN}}$ .

The upshot of the numerical results above can easily be understood on the basis of a symmetry argument. If the spin of the  $x^2-y^2$  hole points along the  $x$ -axis, it is in the spin state  $(|\uparrow\rangle + |\downarrow\rangle)/\sqrt{2}$ , corresponding to  $S^x = 1/2$ . In the intermediate  $2p_{3/2}$  core-hole state the diagonal part of the spin-orbit coupling,  $L^z S^z$ , causes a transition of this spin state into  $(|\uparrow\rangle - |\downarrow\rangle)/\sqrt{2}$  (corresponding

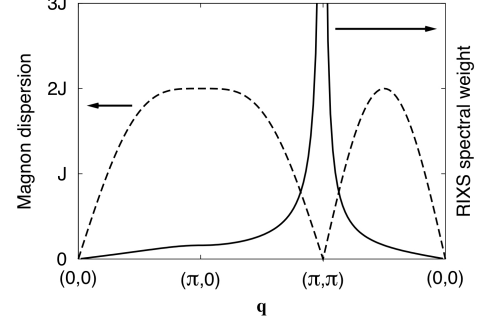


FIG. 3: Momentum dependence of the single magnon spectral weight for RIXS at the copper  $L_3$  edge (solid line) and the magnon dispersion (dashed line) for a simple 2D Heisenberg Hamiltonian

to  $S^x = -1/2$ ), while the angular part of the core-hole wavefunction stays in a linear combination of  $Y_{1,1}$  and  $Y_{1,-1}$ . The transition of the core-hole back into the  $3d$   $x^2-y^2$  orbital is therefore dipole allowed while at the same time the spin along the  $x$ -axis is flipped.

*Momentum dependence of magnon cross section.* We now wish to generalize the cross section from local spin-flips to collective magnetic excitations, which are characterized by their momentum quantum number  $\mathbf{q}$ . There are several ways to compute the  $\mathbf{q}$  dependence of this cross section, but a particularly transparent one is by expanding the Kramers-Heisenberg scattering amplitude formally in a power series of the intermediate state Hamiltonian  $H_{\text{int}}$ :  $A_{fi} = \sum_{l=0}^{\infty} \langle f | \hat{D} (H_{\text{int}})^l \hat{D} | i \rangle / \Delta^{l+1}$ , with  $\Delta = \omega_{\text{det}} + i\Gamma$ , which is the starting point for the ultra-short core-hole life-time expansion for RIXS[14, 23, 24]. The dipole operator  $\hat{D} = \hat{D}_0 + \hat{D}_0^\dagger$ , now allows for a direct creation of a spin-flip upon de-excitation. The corresponding amplitude  $r_{\mathbf{q}}$  depends on polarization, transferred momentum, scattering geometry and initial orientation of the magnetic moment as clarified above and shown in Figs. 1 and 2. We thus obtain

$$\hat{D}_0 = \sum_i e^{i\mathbf{q}_{\text{out}} \cdot \mathbf{R}_i} (1 - r_{\mathbf{q}} + r_{\mathbf{q}} S_i^x) d_i^\dagger p_i + e^{-i\mathbf{q}_{\text{in}} \cdot \mathbf{R}_i} p_i^\dagger d_i$$

where  $d_i^\dagger$  and  $p_i^\dagger$  create a  $3d$  valence hole and  $2p$  core-hole, respectively, and we have taken the direction of the initial magnetic moment as the spin quantization  $z$ -axis. By doing so all magnetic effects of the intermediate state core-hole Hamiltonian have been taken into account so that they can be integrated out and the scattering amplitude is  $A_{fi} = \Delta^{-1} \langle f | \sum_i e^{i\mathbf{q} \cdot \mathbf{R}_i} (1 - r_{\mathbf{q}} + r_{\mathbf{q}} S_i^x) | i \rangle$  with  $\mathbf{q} = \mathbf{q}_{\text{out}} - \mathbf{q}_{\text{in}}$ . The inelastic part of the magnetic scattering amplitude finally reduces to  $A_{fi} = \frac{r_{\mathbf{q}}}{\Delta} \langle f | S_{\mathbf{q}}^x | i \rangle$ .

It is instructive to compute with this generic expression the single magnon RIXS spectrum for, for in-

stance, the antiferromagnetic two-dimensional Heisenberg model, given by the Hamiltonian  $H = J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j$ . Introducing Holstein-Primakoff bosons for  $i$  in sublattice A,  $S_i^z \mapsto 1/2 - a_i^\dagger a_i$ ,  $S_i^+ \mapsto a_i$  and  $S_i^- \mapsto a_i^\dagger$ . For  $j \in B$ , we have  $S_j^z \mapsto b_j^\dagger b_j - 1/2$ ,  $S_j^+ \mapsto b_j^\dagger$  and  $S_j^- \mapsto b_j$ . Adopting linear spin wave theory one finds after a Fourier and a Bogoliubov transformation the magnon scattering amplitude  $A_{fi} = \sqrt{N/2}(u_{\mathbf{q}} - v_{\mathbf{q}}) \langle f | \alpha_{\mathbf{q}} + \beta_{\mathbf{q}} + \alpha_{-\mathbf{q}}^\dagger + \beta_{-\mathbf{q}}^\dagger | i \rangle / \Delta$  with  $N$  the total number of sites and the Bogoliubov transformed boson operators  $\alpha_{\mathbf{k}} = u_{\mathbf{k}} a_{\mathbf{k}} + v_{\mathbf{k}} b_{-\mathbf{k}}^\dagger$  and  $\beta_{\mathbf{k}} = u_{\mathbf{k}} b_{\mathbf{k}} + v_{\mathbf{k}} a_{-\mathbf{k}}^\dagger$ , where  $u_{\mathbf{k}}^2 - v_{\mathbf{k}}^2 = 1$ ,  $u_{\mathbf{k}} = \sqrt{\frac{J}{\omega_{\mathbf{k}}} + \frac{1}{2}}$ ,  $\omega_{\mathbf{k}} = 2J\sqrt{1 - \gamma_{\mathbf{k}}^2}$  and  $\gamma_{\mathbf{k}} = (\cos k_x + \cos k_y)/2$ . The resulting zero-temperature single magnon spectrum is shown in Fig. 3. At  $\mathbf{q} = (0, 0)$  the magnon scattering amplitude vanishes because in this situation the scattering operator is proportional to the total spin in the  $x$ -direction  $S_{\text{tot}}^x$ , which does not cause inelastic processes because this operator commutes with the Heisenberg Hamiltonian. For small transferred momenta,  $|\mathbf{q}| \rightarrow 0$ , the magnon scattering intensity vanishes as  $\omega_{\mathbf{q}}/4J$ . We also observe that the magnon cross section diverges at  $\mathbf{q} = (\pi, \pi)$  as  $4J/\omega_{\mathbf{q}}$ , similar to the neutron scattering form factor. This divergence is due to the RIXS photons scattering on spin fluctuations: at  $\mathbf{q} = (\pi, \pi)$  the scattering operator is proportional to the staggered spin along the  $x$ -axis  $S_{\text{stag}}^x$ , so that the total, energy integrated, scattering intensity  $\int d\omega \sum_f |A_{fi}|^2 \delta(\omega - \omega_{fi}) \propto \langle (S_{\text{stag}}^x)^2 \rangle$  and the inelastic scattering intensity is proportional to the variance  $\langle (S_{\text{stag}}^x)^2 \rangle - \langle S_{\text{stag}}^x \rangle^2$ . In the 2D Heisenberg model the expectation value of these spin fluctuations is proportional to  $N^{3/2}$ .

Using the same formalism, we can compute the  $\mathbf{q}$  dependent scattering amplitude of a spin-flip entangled with a  $dd$ -excitation. If the local spin-flip operator is  $S_i^-$  and the operator corresponding to the  $dd$ -transition is  $T_i^+$ , the inelastic scattering amplitude is  $A_{fi} \propto \langle f | \sum_i e^{i\mathbf{q} \cdot \mathbf{R}_i} S_i^- T_i^+ | i \rangle = \langle f | \sum_{\mathbf{k}} S_{\mathbf{k}}^- T_{\mathbf{k}-\mathbf{q}}^+ | i \rangle$ . Clearly part of the momentum is absorbed by the  $dd$ -excitation, so that RIXS measures a momentum convolution of the two excitations. In particular, the magnetic scattering amplitude loses all  $\mathbf{q}$  dependence if the  $dd$ -excitation is dispersionless, exemplifying that in order to determine magnon dispersions the presence of a *direct* spin-flip process is essential.

**Conclusions.** Depending on the spatial orientation of the copper spin, local spin-flip process for RIXS at the  $L_3$  edge can be forbidden or allowed. This makes RIXS a very sensitive probe of the orientation of the local magnetic moment. In typical cuprates direct spin-flip scattering is allowed and for this case we determined the spin-flip and magnon cross section, which turns out to be strongly momentum and polarization dependent. Our theory holds at both the copper L- and M-edges. At the M-edge ( $\omega_{\text{in}} \approx 75\text{eV}$ ) the photon momentum is small, so that only magnons in a very small portion of the Brillouin

zone can be probed. But at the copper  $L_3$  edge the X-ray photon carries a momentum  $|\mathbf{q}_{\text{in}}| \sim 0.47\hbar \text{ \AA}^{-1}$ , which is in a typical cuprate large enough to observe magnetic excitations in almost all of the Brillouin zone. Indeed in recent high resolution RIXS experiments on  $\text{La}_2\text{CuO}_4$  single magnon scattering features can be discerned [25]. Thus, at least for high  $T_c$  superconductors, L-edge RIXS can be placed on the same footing as neutron scattering –with the additional great advantage that for photon scattering only small sample volumes are required so that the measurement of the spin dynamics of thin films, oxide-heterostructures and other nanostructures comes now within experimental reach.

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